

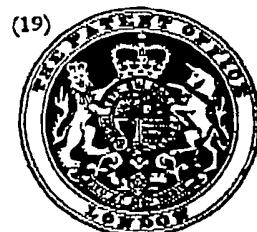
PATENT SPECIFICATION

1 365 503

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 7C10 7C12 7C13P 7C13S 7C16 7C19 7C22 7C24
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 7C8P 7C8R 7L1B 7L2C1 7L2X 7L5D 7L6D
 7L6F 7T2

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(54) AROMATIC POLYMERS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to thermoplastic polymer compositions and in particular to aromatic polysulphones having improved thermal stability.

Aromatic polysulphones and methods for making them are described in British Patent Specifications 1,016,245; 1,060,546; 1,078,234; 1,109,842; 1,122,192; 1,133,561; 1,153,035; 1,153,528; 1,177,183 and 1,234,301, Belgian Patent Specification 741,965, Canadian Patent Specification 847,963, Dutch Patent Specification 70,11346 and Swiss Patent Specification 491,981. They are generally thermoplastic materials of high softening point. Owing to their high softening point, and generally rather high melt viscosities at even higher temperatures, the aromatic polysulphones may tend to decompose as evidenced by an increase in melt viscosity or a darkening in colour unless precautions are taken to stabilise the polymer.

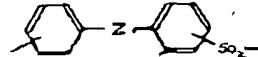
It has now been found that aromatic polysulphones and their blends can be mixed with organic phosphorus compounds to form compositions having improved thermal stability.

According to the present invention a thermoplastic composition is provided comprising (a) 96 to 99.99% by weight of at least one aromatic polysulphone and (b) 4 to 0.01% by weight of at least one organic phosphorus compound having the formula Y_1PQ in which Y is a univalent organic radical which may be the same or different and Q is oxygen or sulphur.

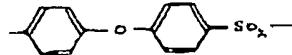
The aromatic polysulphones described in the above-mentioned British specifications comprise repeating units of the formula



in which Ar is a bivalent aromatic radical and may vary from unit to unit in the polymer chain (so as to form copolymers of various kinds). Thermoplastic polysulphones generally have at least some units of the structure



in which Z is oxygen or the residue of an aromatic diol such as 4,4'-bisphenol. One example of such a polysulphone has repeating units of the formula

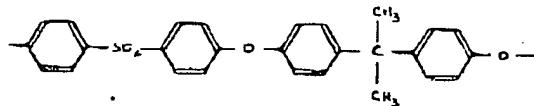


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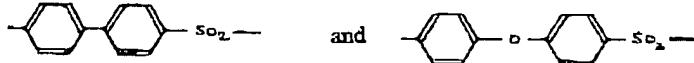
and others (which are commercially available in the United States of America) are said to have repeating units of the formula



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(Union Carbide Corporation) or copolymerised units in various proportions of the formulae

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(Minnesota Mining and Manufacturing Company). Another group of aromatic polysulphones has repeating units of the formula



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alone or copolymerised with any of the above units.

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The organic phosphorus compound has the formula Y_2PQ where Y is a univalent organic radical. Preferably Y is R or OR in which R is any univalent alkyl, aryl, aralkyl or alicyclic group, which may be substituted consisting of up to 20 carbon atoms and Q is oxygen or sulphur. The groups Y may be the same or different in any organic phosphorus compound.

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The compositions of the invention may be made by mixing the organic phosphorus compound with the molten polymer by, for example, extrusion or in a sigma-bladed mixer or in a two-roll mill, or by mixing an aqueous solution of the phosphorus compound with powdered polymer followed by drying.

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The aromatic polysulphone may be blended with other thermoplastic polymeric substances such as, for example, polyesters, polyolefines, polyamides and polyvinyl chloride. The composition may be further mixed with particles of other polymeric materials having special properties, e.g. elastomeric materials and polytetrafluoroethylene. They may contain reinforcing fillers, for example glass, asbestos and carbon fibres, and other materials conferring various desired characteristics, e.g. solid lubricants (e.g. graphite or molybdenum disulphide), abrasives (e.g. carbonundum), friction-reducing materials, magnetic materials (e.g. for recording tapes), photosensitisers, and any other materials for which the compositions of the invention make suitable vehicles. The compositions may contain dyes and pigments. The compositions may be fabricated in any desired form, such as fibre, film and mouldings or extruded products of any desired shape.

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Incorporation of 0.01% to 4% by weight of organic phosphorus compound reduces the tendency of the melt viscosity and colour to increase on prolonged heating of the aromatic polysulphone and its blends. Inclusion of greater quantities appears to have little further effect and may lead to unacceptable opacity in otherwise essentially transparent compositions. A preferred level of inclusion of organic phosphorus compound is 0.01 to 2% by weight.

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The invention is illustrated by the following examples.

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Thermal stability was measured as the increase in melt viscosity (expressed as a percentage) as measured on a ram extruder having a barrel temperature of 380°C or 400°C.

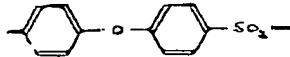
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EXAMPLE 1.

Aromatic polysulphone (100 g) consisting essentially of repeating units of the formula

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made in a manner similar to that described in Example 3 of British Specification 1,153,035 but having a reduced viscosity of 0.48 as measured at 25°C on a solution in dimethyl formamide of 1 g polymer in 100 cm³ of solution was stirred into a solution

of triphenyl phosphate $[(\text{PhO})_3\text{PO}$; 0.5 g] in 190 cm³ of methanol. The mixture was partially dried on a rotary evaporator for 30 minutes at 40° C and finally dried for 20 hours at 150° C. The resulting composition was compression-moulded at 320° C.

The composition showed no increase in melt viscosity after heating at 380° C for 90 minutes whilst untreated polymer showed a 50% increase in melt viscosity and a darker colour after the same heat treatment.

EXAMPLE 2.

In a series of experiments, organic phosphorus compound (0.1 g) was dissolved in a solvent (100 cm³) and mixed with aromatic polysulphone (100 g) similar to that described in Example 1 but having a reduced viscosity of 0.50. The mixture was partially dried on a rotary evaporator for 30 minutes at 40° C and finally dried in an oven for 20 hours at 150° C. Resulting compositions were compression-moulded at 320° C.

The compression-mouldings were granulated and fed into a ram extruder for evaluation of heat stability. The results of melt viscosity examination are presented in the table below together with details of the phosphorus compound and solvent used in the mixing stage.

TABLE

Phosphorus Compound	Solvent	Increase in Melt Viscosity 80 minutes at 400° C (%)
None	None	80
Triphenylphosphine oxide Ph_3PO	Methanol	50
Triphenylphosphine sulphide Ph_3PS	Acetone/methanol 1/2 v/v	35
Tri- <i>p</i> -tolyl phosphate $(\text{MePhO})_3\text{PO}$	Methanol	35
Tri- <i>p</i> -tolyl thiophosphate $(\text{p-MePhO})_3\text{PS}$	Acetone/methanol 1/2 v/v	50
Tri(<i>p</i> -bromophenyl) phosphate $(\text{p-BrPhO})_3\text{PO}$	Ethanol	30

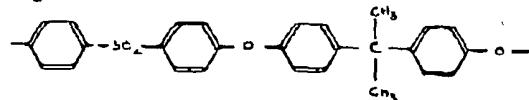
EXAMPLE 3.

Aromatic polysulphone (20 g) similar to that described in Example 1 but having reduced viscosity of 0.41 was stirred into a solution of trioctyl phosphate (0.2 g) in methanol (200 cm³). The mixture was partially dried on a rotary evaporator for 30 minutes at 60° C and finally dried for 60 hours at 120° C. The resulting dry composition was compression-moulded at 320° C.

The compression-moulding was granulated and fed into a ram extruder. The melt viscosity increased by 35% over 70 minutes at 400° C whereas polymer containing no trioctyl phosphate showed a 90% increase in melt viscosity and a darker colour after the same heat treatment.

EXAMPLE 4.

Finely divided triphenyl phosphate (0.1 g) was sprinkled over granules (3 mm long; 3 mm diameter) of "Polysulphone" 1700 (Union Carbide Corporation) (16 g) said to have repeating units of the formula



in a mould and the mixture was compression-moulded at 320° C for 5 minutes.

The compression-moulding was granulated and fed into a ram extruder. There was no increase in melt viscosity after 95 minutes at 400° C whilst after 130 minutes the melt viscosity had decreased by 35% and the extrudate still had good colour. A similar compression-moulding but containing no triphenyl phosphate showed a 25% increase in melt viscosity after 95 minutes at 400° C whereas after 130 minutes the polymer was black and solid and unable to be extruded.

WHAT WE CLAIM IS:—

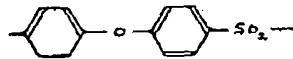
10 1. A thermoplastic composition comprising (a) 96 to 99.99% by weight of at least one aromatic polysulphone and (b) 4 to 0.01% by weight of at least one phosphorus compound having the formula Y₂PQ in which Y is a univalent organic radical which may be the same or different and Q is oxygen or sulphur.

15 2. A thermoplastic composition according to Claim 1 in which Y is a group having the formula R or RO where R is a univalent alkyl, aryl, aralkyl, alkaryl or alicyclic group, which may be substituted, consisting of up to 20 carbon atoms.

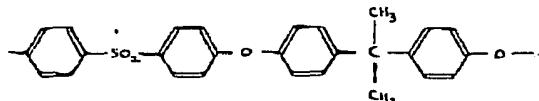
3. A thermoplastic composition according to claim 2 wherein Y is a group having the formula RO and Q is oxygen.

20 4. A thermoplastic composition according to Claim 3 in which the phosphorus compound is triphenyl phosphate.

5. A thermoplastic composition according to any one of Claims 1 to 4 in which the aromatic polysulphone has repeating units of the formula



6. A thermoplastic composition according to any one of Claims 1 to 4 in which the aromatic polysulphone has repeating units of the formula



25 7. A thermoplastic composition according to claim 1 substantially as hereinbefore described with reference to the Examples.

8. A thermoplastic composition according to any one of Claim 1 to 7 in the form of a moulded article.

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